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THE EMISSION BAND SYSTEM OF IODINE IN THE BLUE VIOLET

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Plate I A & B

ABSTRACT. The D—B System of iodine molecule was found to be more extensively developed when the spectrum was excited in a condensed discharge from a high tension transformer. About 150 bands were newly classified as forming part of the previously known D—B system for which Waser and Wieland suggested the vibrational quantum formula.

INTRODUCTION

Recent investigations on the spectra of halogens by Haranath and Rao (1958) have led to the discovery of a number of discrete band systems in the spectral region $\lambda 2400$—$\lambda 1400$. Besides the above new results, a number of previously known systems in the visible and ultraviolet regions were also observed in the case of iodine, when the vapour was excited in a condensed discharge from a high tension transformer. The band system in the blue violet region $\lambda 4400$—$\lambda 4000$ was found to be more extensively developed than has been reported by previous workers. Only 40 bands obtained in fluorescence excitation by Elliot (1940) and about 80 in electrical excitation in the presence of argon by Venkateswarulu (1951) were known previously belonging to this system.

In the present work, the iodine spectrum excited at higher voltages of a condensed transformer revealed about 230 band heads some of which are clearly degraded towards longer wavelengths. This paper describes the results of the detailed investigations on the analysis of this band system attributed to neutral iodine molecule.

RESULTS

Details of the experimental technique employed for the excitation of the emission band spectrum of iodine in a condensed transformer discharge was already described by Haranath and Rao (1958). In the present work, the spectrum extending in the region $\lambda 4500$—$\lambda 3900$ was photographed mainly on Hilger 3 prism glass Littrow and Fuess spectrographs, the times of exposures being of 10 and 5 minutes duration respectively.

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The appearance of the spectrum in the region λ4500—λ3900 photographed on Fuess instrument is shown in three strips *a*, *b* and *c* in Plate IA. They correspond respectively to spectra taken with different primary voltages 60,100 and 140 of the transformer. At the lowest voltage the bands appear sharp and are clearly degraded towards red On increasing the voltage, it was observed that many more new bands appear which are closely spaced. Under these conditions more atomic lines of iodine also appear simultaneously. Plate IB is the reproduction of the spectrum excited with 220 Volts of the primary of the transformer and was recorded on the Littrow spectrograph. Measurements of individual band heads in the region λ4420- λ3965 on a number of plates recorded on the above two instruments agree well with in 2 cm^{-1}. Out of 230 band heads measured in this region, the data of about 80 band heads coincide very well with those reported by Venkateswarulu. In Table I are reported the wavenumber data of the newly recorded band heads about 150 in number with the visual estimates of their intensities

TABLE I

Authors wave number	Int.	Assignment v',v''	Calculated wave number	Obs.—Cal.
22623	1	1,33	22622	+1
22690	2	3,35	22696	−6
22726	1	0,30	22728	−2
22772	3	5,37	22775	−3
22798	1	4,35	22795	+3
22802	1	0,29	22802	0
22823	2	3,33	22823	0
22862	3	2,31	22859	+3
22878	2	0,28	22877	+1
22887	1	3,32	22890	−3
22895	2	5,35	22894	+1
22903	3	1,29	22903	0
22930	1	2,30	22931	−1
22960	3	3,31	22959	+1
22978	1	1,28	22979	−1
23005	3	2,29	23004	+1
23045	4	10,41	23048	−3
23050	6	11,43	23052	−2
23055	4	1,27	23056	−1
23072	4	8,37	23067	+5
23079	4	2,28	23079	0
23089	4	5,32	23089	0
23103	5	3,29	23104	−1
23115	7	0,25	23116	−1
23121	4	6,33	23120	+1
23144	4	11,41	23143	+1
23159	6	2,27	23157	+2
23178	8	3,28	23180	−2

TABLE I (contd.)

Authers wave number	Int.	Assignment v',"v	Calculated wave number	Obs –Cal.
23222	9	9,36	23222	0
23236	8	2,26	23237	–1
23244	10	11,30	23244	0
23284	10	0,23	23284	0
23287	10	7,32	23285	+2
23307	10	5,29	23302	+5
23329	7	6,30	23327	+2
23333	9	3,26	23337	–4
23355	10	4,27	23357	–2
23379	9	8,32	23381	–2
23391	8	12,38	23392	–1
23409	6	9,33	23410	–1
23415	8	11,36	23412	+3
23422	6	7,30	23425	–3
23430	5	13,39	23431	–1
23436	5	4,26	23436	0
23444	10	11,39	23444	0
23450	8	8,31	23450	0
23481	7	9,32	23477	+4
23499	7	3,24	23502	–3
23509	5	12,36	23506	+3
23518	6	4,25	23518	0
23526	8	14,39	23524	+2
23549	8	9,31	23546	+3
23560	7	15,40	23565	–5
23575	2	2,22	23575	0
23609	3	16,41	23607	+2
23653	2	1,20	23655	–2
23664	2	2,21	23665	–1
23676	6	3,22	23675	+1
23687	5	4,23	23687	0
23705	5	19,45	23703	+2
23711	3	6,25	23715	–4
23728	5	13,34	23723	+5
23733	3	7,26	23731	+2
23748	7	1,19	23749	–1
23753	3	14,35	23753	0
23758	3	2,20	23756	+2
23773	5	4,22	23775	–2
23799	2	6,24	23798	+1
23803	2	11,30	23808	–5
23827	8	12,31	23830	–3
23848	2	15,35	23845	+3
23851	3	2,19	23850	+1

TABLE I (ontd.)

Authors wave number	Int.	Assignment v',v''	Calculated wave number	Obs. −Cal.
23874	3	5,22	23874	0
23894	3	7,24	23896	−2
23900	2	12,30	23902	−2
23910	5	8,25	23909	+1
23917	5	20,42	23918	−1
23928	6	13,31	23924	+4
23934	6	16,35	23936	−2
23042	6	1,17	23941	+1
23947	2	2,18	23945	+2
23981	2	7,23	23982	−1
23996	4	13,30	23995	+1
24003	2	9,25	24005	−2
24010	3	20,40	24014	−4
24017	3	10,26	24019	−2
24032	5	11,27	24034	−2
24045	3	3,18	24045	0
24054	2	4,19	24049	+5
24062	2	6,21	24061	+1
24079	4	8,23	24079	0
24092	4	14,30	24088	+4
24115	2	11,26	24114	+1
24126	3	12,27	24128	−2
24145	5	4,18	24145	0
24149	5	5,19	24148	+1
24166	1	8,22	24166	0
24175	4	9,23	24175	0
24206	2	12,26	24208	−2
24223	3	13,27	24222	+1
24237	6	14,28	24237	0
24244	2	1,14	24244	0
24249	2	0,13	24246	+3
24254	2	7,20	24250	+4
24280	2	11,24	24279	+1
24291	2	17,31	24291	0
24302	2	13,26	24301	+1
24345	6	2,14	24344	+1
24350	4	1,13	24346	+4
24379	2	13,25	24383	−4
24396	1	14,26	24394	+2
24407	1	15,27	24406	+1
24422	3	20,33	24422	0
24447	5	3,14	24445	+2
24459	2	12,23	24459	0
24469	3	19,31	24470	−1

TABLE 1 (contd.)

Authors wave number	Int.	Assignment v',v''	Calculated wave number	Obs. − Cal.
24480	1	1,12	24484	−4
24490	2	15,26	24486	+4
24534	5	7,17	24536	−2
24543	5	4,14	24544	−1
24552	4	3,13	24549	+3
24561	4	1,11	24562	−1
24583	2	2,12	24585	−2
24637	3	6,15	24638	−1
24648	3	4,13	24649	−1
24669	1	1,10	24672	−3
24681	1	0,9	24682	−1
24688	1	3,12	24685	+3
24735	2	8,16	24732	+3
24749	1	5,13	24747	+2
24798	1	0,8	24795	+3
24819	2	11,18	24822	−3
24827	2	9,16	24828	−1
24831	3	8,15	24833	−2
24846	3	6,13	24845	+1
24874	2	3,10	24873	+1
24900	1	1,8	24896	+4
24966	2	4,10	24972	−6
24997	1	2,8	24997	0
25015	1	1,7	25011	+4
25032	1	9,14	25031	+1
25043	2	8,13	25040	+3
25071	1	5,10	25071	0
25084	1	4 9	25084	0
25097	1	3,8	25097	0
25112	1	2,7	25112	0
25180	1	5,9	25182	−2
25193	1	4,8	25196	−3
25212	1	3,7	25212	0

ANALYSIS

Waser and Wieland (1947) were the first to propose the following vibrational quantum formula for the bands of iodine molecule in the blue violet region

$$\nu = 25757.2 + (101.88v' - 0.34v'^2) - (126.59v'' - 0.755v''^2 \quad 0.0033v''^3).$$

However, they have not published their experimental data or the vibrational analysis of the bands. Venkateswarulu (1951) reported the classification of about

80 bands of this system on the basis of the above formula. In his analysis the scheme consists of assignments of bands with $v' = 0$ to 11 and $v'' = 9$ to 38. The wavenumbers of these bands are in close agreement with those obtained by the authors. Further, the agreement between the observed and calculated wavenumbers for all the 80 bands is remarkably good. Hence, it is concluded that the vibrational formula proposed by Waser and Wieland represents very well all the 80 bands assigned by Venkateswarulu. However, it is observed that there are a large number of gaps in the vibrational array proposed by him. It is possible to assume that the new bands, 150 in number, obtained in the present investigations could very well form part of this system. On this basis, the above vibrational scheme was extended to include the new bands. It was found possible that all the bands in the region λ4420—λ3965 could be analysed as belonging to a single system whose vibrational formula is the same as that proposed by Waser and Wieland. The vibrational assignments of these new heads were shown in column 4 of Table I. The observed wavenumbers of all these newly assigned band heads were compared with those calculated on the basis of the above formula and their differences were indicated in the last column. The extended vibrational analysis consists of assignments of bands with $v' = 0$ to 20 and $v'' = 7$ to 45.

The intensity distribution of bands of this system is indicated in Table II. It can be seen that most of the strongest bands of the system belong to $v' = 0$ to 6 progressions and the progressions with $v' = 0$ to 5 are more fully developed. The intensity distribution in the system closely corresponds to a typical Condon parabola which is to be expected for values of $\omega_e' = 102.2\text{cm}^{-1}$ and $\omega_e'' = 126.6$

ELECTRONIC STATES

The vibrational constants of the lower state of this system suggest that this is to be identified with the upper state $^3\Pi_{ou}{}^+$ of the visible absorption bands. The upper state of the system was already attributed to the molecular electronic configuration $\sigma_g{}^2\pi_u{}^2\pi_g{}^4\sigma_u{}^2$—$^3\Sigma^-_g$, $^1\Sigma^+_g$, $^1\Delta_g$ of which $^3\Sigma^-_g$ is expected to be lower in energy. These states give rise to $(0_g{}^+, 1_g)$, $0_g{}^+$ and 2_g respectively in Hund's case C coupling. This system designated as D—B was tentatively ascribed to the transition $^1\Sigma_g{}^+(0_g{}^+)$ to $^3\Pi_{ou}(0_u{}^+)$ by Haranath and Rao. Recently Mathieson and Rees have discussed the dissociation products of a group of electronic levels of iodine molecule lying at 40,000 to 55,000 cm^{-1} by consideration of the ionic attractive forces operating. They found that the neighbouring states E and ^1D (D and C according to Haranath and Rao) at ν41411 and ν39293 respectively dissociate into the same products of ions $^3P_2(\text{I}^+)$ and $^1S_0(\text{I}^-)$. They assigned the state at ν41411 the upper electronic level of the blue violet emission band system of iodine to the term $^3\Sigma_g{}^-(0_g{}^+)$ arising out of the configuration (2242). Hence it seems reasonable to assign the D—B system to the electronic transition $^3\Sigma_g{}^-(0_g{}^+)$—

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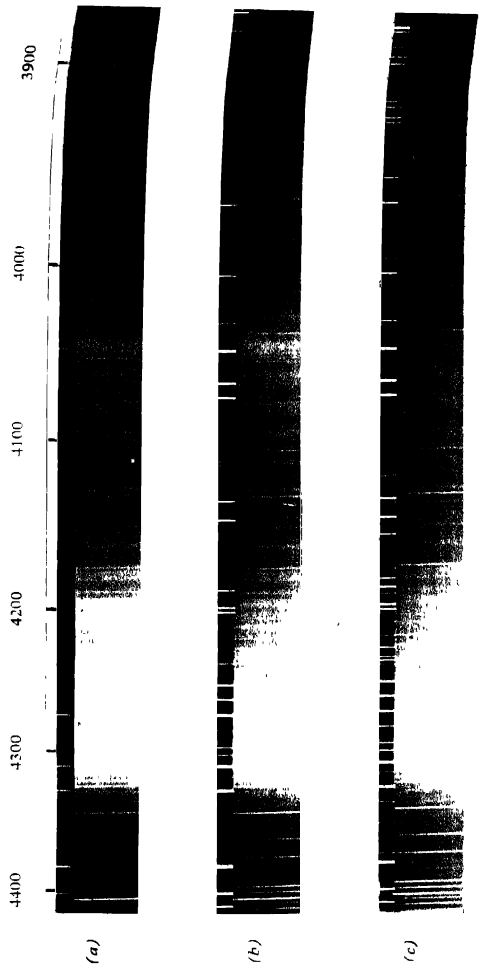
PLATE I A



Emission spectra of iodine excited in condensed discharge from a transformer at different primary voltages Fuess spectrograms (*a*) 60 volts (*b*) 100 volts (*c*) 140 volts.

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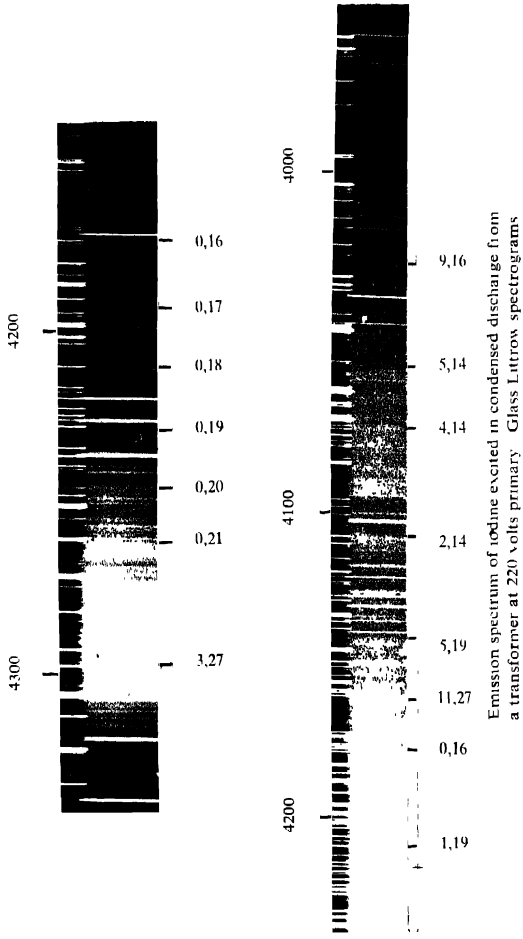
PLATE I



Emission spectrum of iodine excited in condensed discharge from a transformer at 220 volts primary Glass Littrow spectrograms

TABLE II

Intensity distribution of the emission bands system of iodine in the blue violet region

v' \ v''	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
0		1	1	3	2		2	4	4	5	7	7	7	8	8	8	10	9	7	3	3	2	1	1															
1	1	1	2	1	4	1	4	2	4	4	5	7	7	7	7	7	9	10	7	4	4	1	1				1												
2	1	1			1	2	1	6	6			2	3	3	2	2	8	7	7	8	6	4	3	1	2														
3	1	1	2	2		1	4	5	6			3		3	5	6		7	7	9	10	8	5		3	2	2	1	1	1									
4		1	1	2			3	5	5			5	2	4	6	5	5		6	5	7	10							1	1									
5			1	1			1	3		5			5			3	6		3	8			10	9		5			2		2								
6							2	3	3	5					2	3	3	2	3					7	10	8	4													
7							3	3			5			2		2	2	3	2	5				6		10		6												
8							2	2	3	3	3					1	4	4	5				2		8	9		9			4	3								
9								1		2					4		4	4	2	5					8	7	8	9		9		6								
10										2		2					2			3							5	9						5	4					
11												2						2	5	2	5			2						6			10		4		6		
12																	2			2	3			2	8					5		8							
13																			2	2	3			4	6			5					5						
14																				1		6		4	3				3				8						
15																				2	1	4			4			5	2					7					
16																										3			6						3				
17																									2														
18																																						
19																									3											6		5	
20																												3						3		6			

$^3\Pi_{0g}+(0_g^+)$ in which case the selection rules of Hund's cases *C* and *B* coupilngs hold good smultaneously

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